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博士后学位论文

以钆基化合物为工质的磁制冷循环性能特性的研究

The study on the performance characteristics of magnetic refrigeration cycles using Gd-based compounds as the working substance

DIGUET Gildas

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摘　要

基于Gd基室温磁制冷材料的等磁场热容量随温度变化的实验数据，获得相应的等场熵温曲线，进而建立以这些材料为工质的回热式Brayton/Ericsson制冷循环。应用热力学分析和数值计算方法，揭示非平衡回热对Brayton/Ericsson制冷循环主要热力学性能的影响。进一步深入讨论不同温区的非平衡回热，同时对这两种材料的循环性能进行比较。研究结果可为室温磁制冷机循环的优化设计提供参考。

关键词：磁性材料；制冷；回热；循环性能

Abstract

Based on the experimental characteristics of the iso-field heat capacity changing with temperature for the room-temperature magnetic refrigeration materials Gd, Gd0.74Tb0.26, and (Gd3.5Tb1.5)Si4, the corresponding entropy versus temperature curves are calculated and presented, the regenerative magnetic Brayton refrigeration cycles, using these magnetic materials as the working substances, are established. The nonperfect regenerative heat quantity, net cooling quantity, released heat quantity, coefficient of performance (COP) and other performance parameters of these magnetic Brayton refrigeration cycles are analyzed and calculated. Furthermore, the performance characteristics of the Brayton refrigeration cycles employing Gd, Gd0.74Tb0.26, and (Gd3.5Tb1.5)Si4 as the working substance are evaluated and compared, the influence of nonperfect regenerative heat on the performance characteristics of these magnetic Brayton refrigeration cycles is revealed.

The cycle model of an irreversible regenerative magnetic Brayton refrigerator using Gd0.74Tb0.26 as the working substance is established. Based on the experimental characteristics of iso-field heat capacities of the material Gd0.74Tb0.26 at 0T and 2T, the corresponding iso-field entropies are calculated and the thermodynamic performance of an irreversible regenerative magnetic Brayton refrigeration cycle is investigated. The effects of the irreversibilities in the two adiabatic processes and non-perfect regenerative process of the magnetic Brayton refrigeration cycle on the cooling quantity, the heat quantity released to the hot reservoir, the net cooling quantity and the coefficient of performance are discussed in detail. Some significant results are obtained.

Based on Mean Field Theory (MFT), the entropy of magnetic material Gadolinium (Gd), which is a function of the local magnetic field and temperature, is calculated and analyzed. This local magnetic field is the sum of the applied field H0 plus the

exchange field $H_W = \lambda M$ and the demagnetizing field $H_d = -NM$, where the demagnetizing factor N depends on the shape of magnetic materials. Hereby, the impacts of the demagnetizing factor N on the magnetic entropy, magnetic entropy change and main thermodynamics performance of a regenerative magnetic Brayton refrigeration cycle using Gd as the working substance are investigated and evaluated in detail. The results obtained underline the importance of the shape of the working substance used in magnetic refrigerators for room-temperature application; elongated materials provide better thermodynamics performance such as higher COP and net heat absorption. It is pointed out that for low external fields, the magnetic refrigerator ceased to be functional if flat materials were used.

Thermodynamic performance analysis for a magnetic composite material in a regeneration Ericsson refrigeration cycle is then presented. The regeneration heats in the two regenerative processes of the Ericsson refrigeration cycle are usually non-perfect and this non-perfect regenerative quantity is calculated and analyzed. Furthermore, from the experimental data of iso-field heat capacities of Gd, $Gd_{0.74}Tb_{0.26}$, and $(Gd_{3.5}Tb_{1.5})Si_4$, thermodynamic performance of the corresponding composite material, based on these materials, in a regeneration Ericsson refrigeration cycle is evaluated and analyzed. Due to the non-perfect regeneration, the composite cooling quantity and coefficient of performance of the Ericsson refrigeration cycle decrease, but they are still larger than those of each of its compounds. The calculation method of the magnetic composite presented here can be used as a new basis for creating a new magnetic composite with better regeneration processes in the Ericsson refrigeration cycle.

A method to obtain the iso-field heat capacity and/or entropy, from experimental iso-thermal change of entropy and adiabatic temperature change curves, is then obtaiened. This calculation is performed in two steps and then combined to extract the expected data. The first step is the iso-field heat capacities direct calculation while the second step consists in the direct iso-field entropies calculation. Both of these two steps are then analyzed to avoid their respective errors and to keep their respective advantages. The combination shows a remarkable agreement with experimental curves.

Based on the experimental isothermal entropy change of the magnetic materials GdxDy1-x, the thermodynamic performance of a regeneration Ericsson refrigeration cycle is evaluated and analyzed. The effects of non-perfect regeneration on the cyclic performance are highlighted. For a room temperature hot reservoir, the cooling quantity, non-perfect regeneration heat quantity, and net cooling quantity of the established regeneration Ericsson refrigeration cycle are calculated as function of the cold reservoir temperature. Furthermore, for several typical compositions x of the GdxDy1-x alloys, the values of the cooling quantity, non-perfect regeneration heat quantity, work input, net cooling quantity, and coefficient of performance (COP) are listed for given temperatures of the cold reservoir. The cyclic performance of the GdxDy1-x alloys with different composition x is compared and some significant analyses are provided.

The magnetic field effect on the thermodynamics properties of a Magneto Caloric Material used as the working substance within regeneration magnetic refrigeration Brayton and Ericsson cycles. Based on the experimental iso-field heat capacities of Gd at various magnetic fields, the complete description of the field effect on thermodynamics properties such as the entropy change, cooling heat quantity, regenerative losses and the net cooling quantity is provided. This analysis revealed possibility to reduce the regenerative losses and to improve the net cooling quantity for a given field change by selecting the best initial and final field values. The coefficient of performance is then also positively affected. These calculations of thermodynamics properties are then applied to a second Magnetic material, namely $Gd_{0.87}Dy_{0.13}$.

Keywords: Magnetic material; Magnetocaloric effect; Room-temperature magnetic refrigeration

参考资料

[1] R. Konig. International Journal of Refrigeration 23(2000) 577-587

[2] B. Yu, M. Liu, P.W. Egolf, A. Kitanovski. International Journal of Refrigeration 33 (2010) 1029-1060

[3] O. Tegus, E. Bruck, K. H. J. Buschow & F. R. de Boer. Nature vol 415 (2002) 150

[4] E. Bruck, O. Tegus, F. R. de Boer, K. H. J. Buschow, X.W. Li. Physica 327 (2003) 431-437

[5] K. A. Gschneidner Jr, A. O. Pecharsky. International Journal of Refrigeration 31(2008) 945-961

[6] V.K. Pecharsky, K. A. Gschneidner Jr. JMMM 200 (2003) 44-56

[7]A.M. Tishin, A.V. Derkach, Y.I. Spichkin, M.D. Kuz ’ min, A.S. Chernyshov, K.A. Gschneidner Jr., V.K. Pecharsky. JMMM 310 (2007) 2800-2804.

[8] H. Oesterreicher, F.T. Parker. J. Appl. Phys. 55(12) 1984 4334-4338

[9] B. Yu, Q. Gao, B. Zhang, X.Z Meng, Z. Chen. International Journal of Refrigeration 26 (2003) 622-636.

[10] N.A. de Oliveira, P.J. vopn Ranke. Physics reports 489 (2010) 89-159

[11] A. Kitanovski, P.W. Egolf. International Journal of Refrigeration 29 (2006) 3-21

[12] V.K. Pecharsky, K.A. Gschneidner Jr., A.O. Pecharsky, A.M. Tishin. Phys. Rev. B 64, (2001) 144406.

[13] T. Hashimoto, T. Numasawa, M. Shiino. Physica B+C vol.108 issue 1-3 (1981) 1107-1108

[14] T. Hashimoto, T. Numasawa, M. Shiino. Cryogenics 20 (1981) 647-653

[15] M. Balli, D. Fruchart, D. Gignoux, E.K. Hlil, S. Miraglia, P. Wolfers. Journal of Alloys and Compounds 442(2007) 129-131

[16] Y.I. Spichkin, V.K. Pecharsky, K.A. Gschneidner. J. Appl. Phys. Vol. 89, no.3 (2001) 1738-1745

[17] Z. Dia, P. Zhang. B. Qian, X. Jiang, D. Wang, J. Chen, J. Feng, Y. Du. Journal of Alloys and Compounds 504 (2010) 310-313.

[18] D. Wang, Z. Su, S. Huang, Z. Han, W. Zou, Y. Du. Journal of Alloys and Compounds 387 (2005) 6-8

[19] M.H. Phan, S.B. Tian, D.Q. Hoang, S.C. Yu, C. Nguyen, A.N. Ulyanov JMMM 258-259 (2003) 309-311

[20] M.D. Kuz ’ min. Physical Review B 77, 184431 (2008)

[21] Z.G. Zheng, H.Y. Yu, X.C. Zhong, D.C. Zeng, Z.W. Liu. International Journal of Refrigeration 32 (2009) 78-86

[22] M. Risser, C. Vassile, T. Engel, B. Keith, C. Muller. International Journal of Refrigeration 33(2010) 973-981

[23] C. Aprea, A. Greco, A. Maiorino. Energy Conversion and Management 52 (2011) 92-107

[24] D.S. Arnold, A. Tura, A. Rowe. International Journal of Refrigeration 34(2011) 178-191

[25] Z. Yan, J. Chen. J. Appl. Phys. 69 (9) 1991

[26] Z. Yan, J. Chen. J. Appl. Phys. 72 (1) 1992

[27] G. Lin, O. Tegus, L. Zhang, E. Bruck. Physica B 344 (2004) 147-156

[28] Z. Xia, Y. Zhang, J. Chen, G. Lin. Applied Energy 85 (2008) 159-170

[29] Z. Xia, X.M. Ye, G.X. Lin, E. Bruck. Physica B 381 (2006) 246-255

[30] X.M. Ye, G.X. Lin, J.C. Chen, E. Bruck. Physica B 391 (2007) 350-356

[31] X. Zhang, J. Chen, G. Lin, E. Bruck. Physica B 405 (2010) 1632-1637